Rate of Reaction of Oxygen and Steam with Char/Coke[*]

Satyendra P. Nandi, Robert Lo and Jack Fischer

Chemical Engineering Division, Argonne National Laboratory

Argonne, Illinois 60439

In most coal gasification processes, raw coal is initially subjected to heat treatment. Even in the presence of reactive gases the initial rapid weight loss of the coal can be ascribed primarily to devolatilization. The resultant char is then converted to desired products in subsequent steps. It is believed that the gasification of the char is the slow step in the overall conversion reactions. The overall char gasification process consists of a number of reactions, amongst them the steam-carbon and oxygen-carbon reactions are the most important. The steam-carbon reaction

$$C + H_2O \rightarrow CO + H_2 \qquad \qquad 1)$$

is endothermic and its rate does not become significant below about 750°C. The heat required by reaction 1) can be supplied by the highly exothermic carbon-oxygen reaction

$$C + O_2 \rightarrow CO_2 \text{ and } CO \qquad \qquad 2)$$

The CO/CO_2 ratio is a function of temperature and carbon monoxide is favored at higher temperatures. Depending on the nature of carbon, the rate of this reaction may become significant at a temperature as low as 350°C. In the overall gasification scheme, judicious combinations of reactions 1) and 2) are used. It is therefore necessary to obtain a measure of the rates of these two reactions using various chars made from coals which are practical for use in gasifiers.

Various workers (1) have studied the carbon-steam and carbon-oxygen reactions using graphites. Because of the pronounced difference in inherent reactivity of the two gases, it is rather difficult to obtain values of the reactivity of a char for the two reactants at the same temperature. Similar data for graphite are scanty. Jenkins et al. (2) determined the reactivity parameter, defined later in this report, for a series of coal chars in air at 500°C. All the chars in Jenkins' work were prepared by heating various types of coal in nitrogen at a heating rate of 10°C/min to a maximum heat-treatment temperature of 1000°C. The results showed that the reactivity of the char was a function of the rank of the parent coal; the low-rank coals produced chars of much higher reactivity. It was also shown that the value of the reactivity parameter was the same, whether the chars were produced in a thermobalance (static bed) in milligram quantities or in a fluid bed in gram quantities.

In our work the approach taken was to measure the rates of char-steam and char-oxygen reactions over a range of temperature, determine the temperature coefficient of rates (apparent activation energy) of the separate reactions, and estimate the value of the relative rates at a common temperature. The magnitude of the apparent activation energy when compared with the values reported for pure carbon may indirectly provide some insight into the mechanisms of both the reactions.

EXPERIMENTAL

The porous nature, particle size, and maximum heat-treatment temperature of the char, the rank of the parent coal, and the inorganic matter present in the char are the variables which may affect the rate of the char-oxygen or char-steam reaction. The rate of heating used in preparation of the char is expected to affect the porous nature and is not considered as a separate variable. In this work the particle size, heating rate, and the maximum heat-treatment temperature are kept invariant.

Samples

Four samples of coal were selected for this work. Three coals are of low rank (subbituminous or lower) and the fourth is of MVB rank. There are vast resources of subbituminous coals in Western U.S., and their gasification behavior is of interest. The MVB sample was included for comparative purposes.

The analyses of the samples are shown in Table 1.

Experimental Procedure

The coal samples were pyrolysed in a tube furnace in a flow of nitrogen with a heating rate of 8°C/min to a maximum temperature of 900°C and held at that temperature for two hours. The coal samples were sieved and the fraction (35 x 80) mesh Tyler was used. The particle size of the char is expected to be somewhat smaller. On pyrolysis, sample 274 produced a coke mass, this was crushed, and a sieved fraction of (35 x 80) mesh was used for the reactivity determination.

The reactions were carried out using a thermobalance. A char sample was spread uniformly in a shallow platinum thermobalance pan. The amount of sample used, ∿10 mg, was such that the bed was about one particle diameter high. The samples were initially brought to the reaction temperature in nitrogen and after steady weight was attained, the reactive gas was introduced. Dry air was used for oxygen reactivity measurements. Pure nitrogen was passed through a series of bubblers containing distilled water to obtain a partial pressure of 2.3 volumn per cent of water vapor in the stream. This mixture was used to determine the rate of the steam-char reaction. The reaction was followed isothermally by means of a thermobalance and the rate was calculated from the weight loss. The flow rate of the reactive gas was kept constant and was such that the supply of the reactive gas was two orders of magnitude greater than could be consumed when the rate of carbon loss was at the maximum. The temperature range for the oxygen-char reaction was from 350 to 575°C and for the steam-char reaction, from 750 to 900°C.

(a) Char-Oxygen Reaction

The percent weight loss based on the weight of original sample of char on a dry ash-free basis as a function of time for 274 coke is shown in Fig. 1. The low rate observed during the initial period is partially due to the time required for the air to replace the nitrogen from the vicinity of the carbon. This period is longer at lower temperature, which indicates that there is an induction period (the gas flow rate being the same in all cases). The induction period in carbon-oxygen reaction had been explained (3) by assuming that initially oxygen becomes chemisorbed on the surface. This is followed by subsequent desorption of the bound oxygen as oxides of carbon. With the removal of carbon from the surface, the char remaining increases in porosity, i.e., its specific surface area increases. From similar arguments, the middle linear portion of Fig. 1 can be regarded as a region where the opposing effects of carbon removal and generation of extra surface area are in balance. When the

carbon loss is high, the absolute value of the total reactive area is decreased, and consequetnly, the rate falls off. In this work, the middle linear portions of the experimental curves are used to calculate the characteristic rates.

The reactivity parameter was calculated by the following equation

$$R_{max} = \frac{1}{w_o} \ \frac{dw}{dt}$$

where R_{max} = maximum reactivity at the experimental temperature expressed as mg of char reacted per minute per mg of initial sample; w_o = initial mass of the char on dry ash-free basis and $\frac{dw}{dt}$ = maximum rectilinear weight loss rate (mg. min^{-1}). The approach taken to obtain R_{max} is the same as that of Jenkins et al. (2)

The weight loss data for the air-char reaction for the other samples are shown in Figs. 2 to 4. The calculated values of R_{max} are shown in an Arrhenius plot in Fig. 5. The reactivity of the coke sample (sample 274) was much lower compared with those for the char samples. It is also observed that the plots for char/coke from 274, 248 and 247 are straight lines in the temperature interval. The values of the apparent activation energy are nearly the same (~21 kcal/mole) for these three samples.

Values of the activation energy for the carbon-oxygen reaction (1) using pure carbon (graphite) have been reported to be in the range of 37 to 58 kcal/mole. The value, 36.7 kcal/mole, was obtained by Gulbersen and Andrew, (4) who reacted thin spectroscopic graphite plates between 425 and 575°C under 0.1 atmosphere of oxygen. The much smaller values of the apparent activation energy obtained in this work indicate that (i) catalysis by inorganic matter in the char occurred and/or (ii) the reaction occurred inside small pores whose length are much greater than their diameter. In the latter case Wheeler (5) had shown that the apparent activation energy will be equal in magnitude to half the value of the true activation energy of reaction. The nature of the minerals present in the chars was not determined. However, the possibility appears unlikely that the minerals were similar in nature or that they catalyzed the reaction in such a way as to produce the same apparent activation energy for the three materials. This strongly suggests that the reaction is being controlled by pore diffusion. The Arrhenius plot for the LLL char is not linear. Initial reactivity of this sample is very high and the curvature in the plot indicates that the reaction at high temperature, for this sample, is being partially controlled by bulk diffusion.

(b) Steam-char reaction

The experimental data for this reaction are presented in Figs. 6 to 9. The initial period of low reaction rate is of much lesser duration than in the oxygen-char reaction. It has been reported (1) that the steam-carbon reaction also proceeds through a chemisorbed oxygen intermediate, which may be of a different nature than that in the carbon-oxygen reaction. The much higher temperature used for the carbon-steam reaction may contribute to a rapid build-up of a steady-state concentration of chemisorbed species on the surface, resulting in a shorter induction period. A linear rate of weight loss over an extended reaction range is then obtained in all cases. This linearity results from the same opposing factors identified earlier for the char-oxygen reaction.

The shape of the curves shown in Figs. 7 to 9 are similar and show a qualitative resemblence to the curves obtained in char-air reaction. The data for the

coke shown in Fig. 6 are quite different. Two distinct linear regions are observed. A possible way of explaining the data is to assume a small fraction of disorganized carbon is mixed in with the relatively well-ordered carbon of the coke. After the fast reaction of the disorganized carbon has been completed, the rate falls to a value that is characteristic of the well-organized carbon.

The R_{max} values for the steam-carbon reaction have been calculated from the data in Figs. 6 to 9 in a way similar to that used for the air-carbon reaction calculations. These data are shown graphically in Fig. 10. The values of the apparent activation energy for the 274 coke are based on limited data; the slope obtained at the low rate is about half of that at the high rate. The value of the apparent activation energy calculated from the low rate is ~82 kcal/mole, which is in the neighborhood of the value (80 kcal/mole) reported for the graphite-steam system. (1)

The carbon contents of coals 247 and LLL are not very different. The apparent activation energy values obtained for the chars of these two coals are nearly the same (23 and 27 kcal/mole). The value for sample 248 was somewhat higher, ~42 kcal/mole. This sample belongs to SubbC rank of coal. The ash content of this sample was lower than that of 247 and LLL samples.

This low value of the apparent activation energy indicates that the reaction studied in this work probably proceeded by a different mechanism than that for graphite-steam reaction. Wheeler's explanation for the difference in the magnitude of the activation energy for the same reaction taking place inside long narrow capillary, and on a plain surface has been mentioned earlier. It appears that for the three char samples, the major part of the reaction could be occurring inside narrow pores. In addition, the reaction may be influenced by catalytic impurities in some cases.

(c) Relative reactivity in oxygen and steam

Walker et al., (1) in their review of the gas-carbon reaction reported that the rate of carbon-oxygen reaction was 3×10^4 times as rapid as that of the carbon-steam reaction under equivalent conditions (temperature = 800°C, pressure of gas = 0.1 atm). The experimental results used in the above estimation were obtained primarily with graphite. From the experimental data obtained in this work for 247 char, the relative rates of oxygen to steam reaction were calculated using the computational method of Walker et al. For this sample the ratio of the rates of oxygen to steam reactions was found to be only ~24 · (T = 800°C and P = 0.1 atm). The reactivity ratio for the LLL char would be even lower because the slope of the Arrhenius plot (char-air) for this sample decreased at higher temperature. It is concluded that the reactivity ratio of oxygen to steam reactions with coal chars will be much lower than that expected for pure forms of carbon.

Table 1

Analyses of Coal

Sample No.	ASTM Rank	Percent as received			Percent dry ash basis				
		Moist.	Ash.	Wt. loss to 900°C	C	H	N	S	O (by diff)
274	MVB	1.42	1.75	27.2	86.30	4.32	–	1.2	–
248	SbbC	16.67	2.48	51.4	75.16	5.15	1.73	0.66	17.26
247	L	14.10	6.52	50.2	74.43	4.91	1.49	0.53	18.62
LLL	L	29.60	6.50	59.1	74.34	5.52	1.18	0.45	18.51

REFERENCES

1. P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, Adv. Catal., Vol. 11, Academic Press, New York, 1959, pp. 134-217.

2. R. G. Jenkins, S. P. Nandi, and P. L. Walker, Jr., Fuel 52, 288 (1973).

3. B. G. Tucker and M. F. R. Mulcahy, Trans. Faraday Soc., 65, 274 (1969).

4. E. A. Gulbersen and K. F. Andrew, Ind. Eng. Chem. 44, 1034 (1954).

5. A. Wheeler, Adv. Catal., Vol. 3, Academic Press, New York, 1951, pp. 250-326.

Figure 2. Rate of reaction between AIR and 248 CHAR
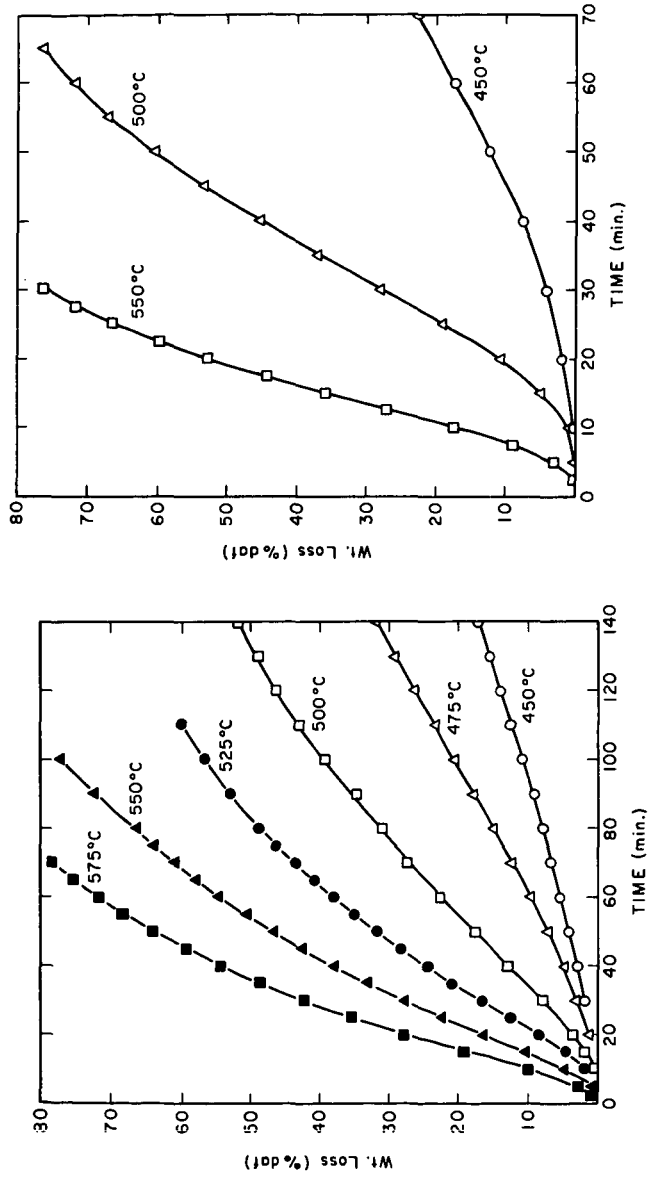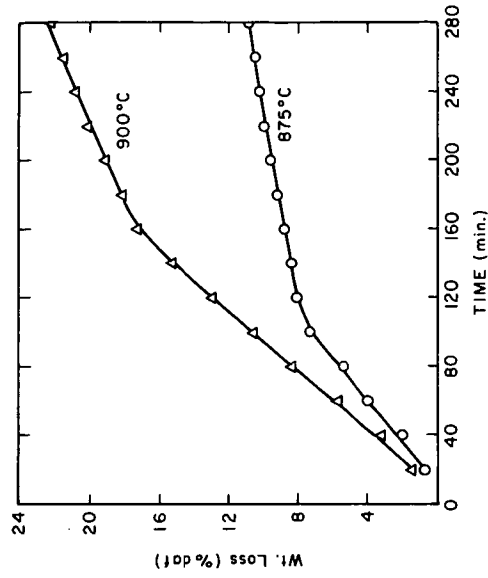
Figure 1. Rate of reaction between AIR and 274 COKE
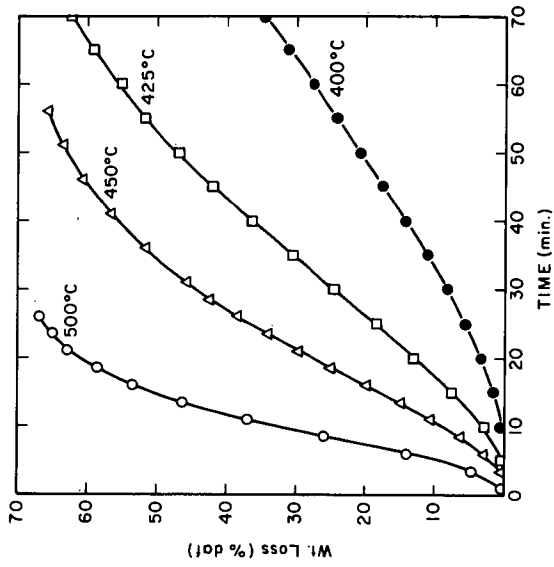
Figure 4. Rate of reaction between AIR and 247 CHAR
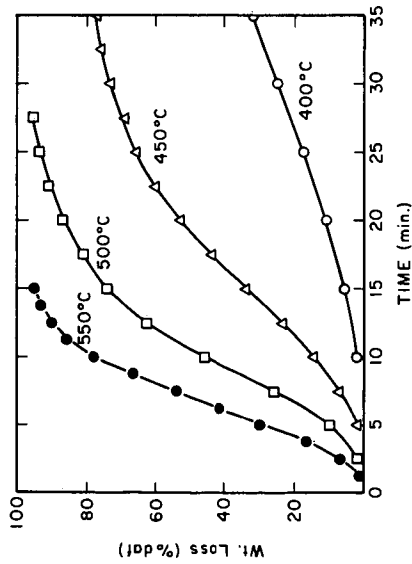
Figure 3. Rate of reaction between AIR and LLL CHAR

Figure 6. Rate of reaction between 2.3% STEAM and 274 COKE

Figure 5. Arrhenius Plot - Maximum reaction rate in AIR - CHAR/COKE system
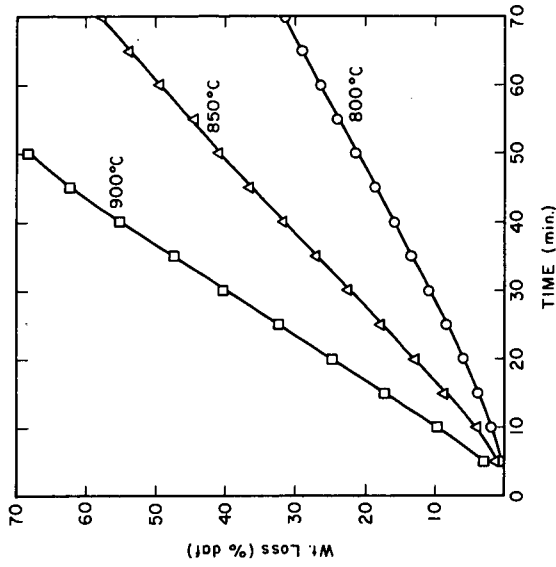
Figure 8. Rate of reaction between 2.3% STEAM and LLL CHAR
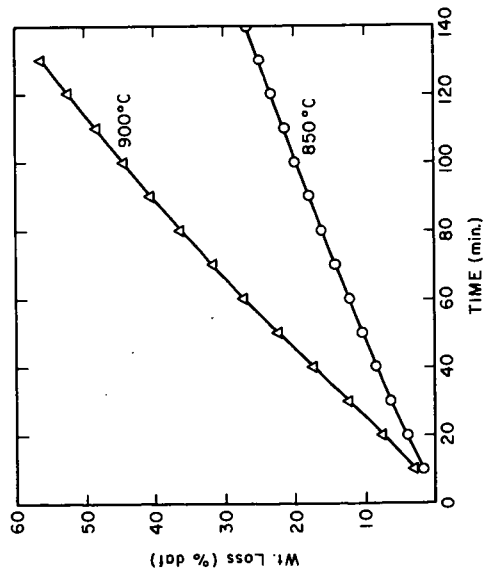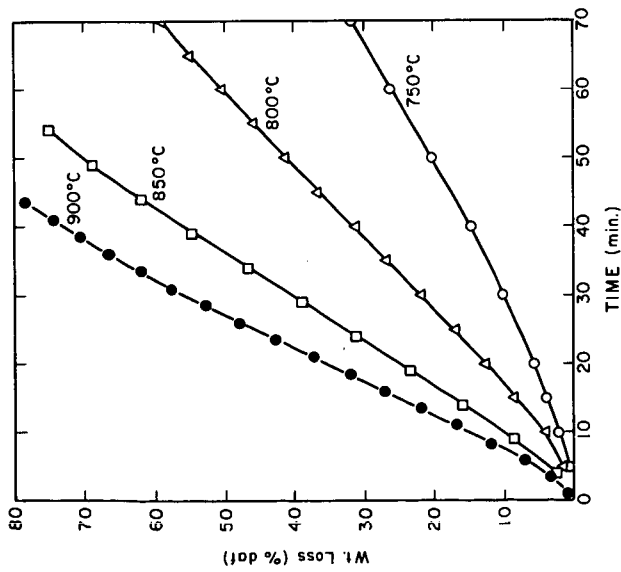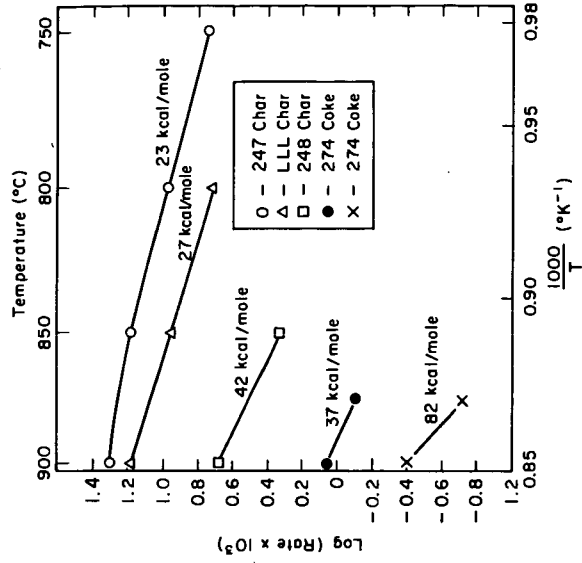
Figure 7. Rate of reaction between 2.3% STEAM and 248 CHAR

Figure 10. Arrhenius Plot - Reaction rate in STEAM - CHAR/COKE system

Figure 9. Rate of reaction between 2.3% STEAM and 247 CHAR